(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 30 August 2001 (30.08.2001)

PCT

(10) International Publication Number WO 01/62670 A1

(51) International Patent Classification?: // 101/10

C02F 1/28

- (21) International Application Number: PCT/GB01/00822
- (22) International Filing Date: 26 February 2001 (26.02.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 0004579.9 25 Feb

25 February 2000 (25.02.2000) G

- (71) Applicant (for all designated States except US): CAPITAL CONTROLS LTD [GB/GB]; Park Lane, Minworth, Sutton Coldfield, West Midlands B76 9BL (GB).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): SIMMS, John [GB/GB]: Severn Trent Water Ltd, Avon House, St. Martin's Road, Coventry CV3 6PR (GB).
- (74) Agents: KIRKHAM, Nicholas, Andrew et al.; Graham Watt & Co., Riverhead, Sevenoaks, Kent TN13 2BN (GB).

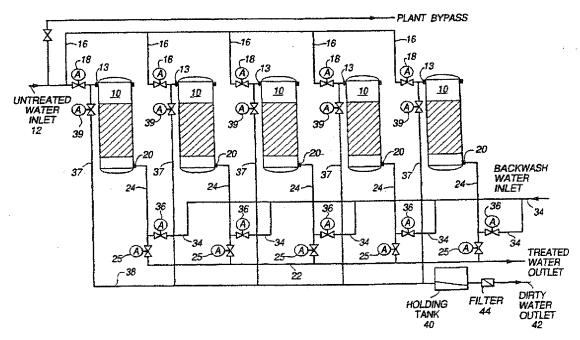
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CÜ, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: APPARATUS AND METHOD FOR WATER TREATMENT BY ADSORPTION



(57) Abstract: The present invention relates to an apparatus and method for removal of arsenic or other metal salts from drinking water. The invention uses a bed of granulated ferric hydroxide to adsorb the metal in a pressurized adsorption chamber. The bed is sized to about 10 m³ and run with an EBCT of about 3 minutes which has been found to give an unprecedently long bed life of upto 200,000 bed volumes of treated water.

01/62670 A1

APPARATUS AND METHOD FOR WATER TREATMENT BY ADSORPTION

The present invention relates to a method and apparatus for arsenic or other metal removal from water, in particular but not exclusively, potable ground water.

Ground water represents an important source of drinking water but has been found to contain dissolved metal ions such as arsenic, copper, nickel, chromium, lead, cadmium, molybdenum, silver, mercury and manganese, often at undesirable levels.

For example, recent regulations have stipulated that the level of arsenic should be less than $10 \,\mu\text{g/l}$. Arsenic and other metals may be removed from water by using one or more of the following methods; (i) adsorption by activated aluminium, (ii) nanofiltration, (iii) in a clarification/filtration plant using overdosing coagulation; or (iv) ion exchange. Each of these processes has disadvantages. Activated aluminium has a limited adsorption capacity. Nanofiltration allows comparatively slow processing rates. The construction of a coagulation plant has a high capital cost due to e.g. the large amount of land required and high operating costs.

The present invention seeks to provide an advantageous apparatus and method for the removal of metals.

According to a first aspect of the present invention there is provided an apparatus for removing metals from water comprising an adsorption chamber including a bed having a bed height and comprising a ferric material, a water inlet connectable to a first water supply on one side of the bed, a water outlet on the other side of the bed and a backwash inlet connectable to a second water supply on the said other side of the bed, the apparatus being arranged for normal and backwash operations, in normal operation arsenic

5

10

15

20

25

is adsorbed onto the bed from water flowing from the said one side to said other side, and in backwash operation water flows from the backwash inlet to said one side of the bed, the bed height is between 0.5m and 2.0m and the empty bed contact time (EBCT) is between 1 and 6 minutes.

5

According to a second aspect of the present invention there is provided a process for removing metal from water comprising the steps of:

a) providing a bed of ferric material having a bed height of between 0.5 and 2.0m;

10

b) in normal operation supplying water from a first water supply from one side of the bed to the other side of the bed such that arsenic is adsorbed from the water onto the bed;

15

c) in backwash operation supplying water from a second water supply from said other side of the bed to said one side of the bed so as to remove contaminating material from the bed without substantially disrupting the media; wherein in normal operation, the empty bed contact time for said water is between 1 and 6 minutes.

20

25

The present inventors have found that using a bed of ferric adsorption media allows increased metal adsorption when compared to activated aluminium (wt/wt) with the consequential reduction in the cost associated therewith. Surprisingly, given the fragile nature of the bed, a long interval between backwashing cycles is possible without clearly increasing the differential pressure across the bed and/or without significant reduction in the adsorption rate and capacity of the bed. Furthermore the bed of adsorption material required by the present invention is made from a material which is relatively fragile in nature and so has been proportioned to allow the bed to be formed by educting the material into the adsorber without the bed material being disrupted. Yet the bed maintains sufficient size to allow the treatment of commercial volumes of water. Surprisingly, it has been found that the adsorption bed of the invention can treat an unprecedently large

volume of water before replacement i.e. when it reaches the allowed/set limit for the metal being removed from the water, e.g. in the case of arsenic the treated water having $10\mu g/l$ arsenic. The bed size in conjunction with the EBCT provide an adsorber with a high capacity, yet the bed size is not so great to cause logistical problems in maintaining the bed. This is important as the apparatus may well be in a remote location where complicated and/or frequent maintenance would greatly increase costs for the process. The adsorption bed of the present invention should not need to be replaced more frequently than once per annum which is considered to be commercially acceptable given the cost of the material.

Preferred features of the invention have been given in the dependent claims.

The preferred features have each been found to improve the cost efficiency of the plant and may be used together or individually.

15

5

10

The use of a ferric adsorption material was also found to allow relatively high rates of metal adsorption and a reduction in the capital expenditure required to build a plant when compared to a sludge plant.

20

Ferric oxide and hydroxide containing natural materials have been found to be both relatively cheap to use and to give satisfactory adsorption efficiencies e.g. the ability to adsorb large quantities of arsenic, typically 1.3g to 3.5g of arsenic is removed per Kg of Ferric Hydroxide. The use natural material containing these two compound has been found to give high economy and high adsorption.

25

Advantageously according to the first and second aspects of the present invention a layer of gravel separates the media from the support base. Gravel has been found to be an economic inert material to use which is widely available.

Advantageously according to the first, second and third aspects of the invention the pH use is in the range of 6.5 to 8.5, particularly 7.0 to 8.0. The adsorption of arsenic is satisfactory within this Ph range and normally this means that no adjustment to the Ph is required for processing greatly reducing the cost and complexity of the operating condition which latter advantage is very important given the plant is normally unmanned.

The invention will now be described with reference to the accompanying drawings, in which:

10

20

25

30

5

Figure 1 is a schematic illustration of a arsenic adsorption plant according to the present invention;

Figure 2 shows a vertical cross sectional view through an adsorber according to Figure 1; and

15 Figure 3 shows a horizontal cross sectional view of an adsorber according to Figure 1.

The present invention is exemplified with the following description and drawings which show an arsenic adsorption plant. The invention is not limited to arsenic adsorption, but this is the preferred embodiment of the invention.

Figure 1 shows a plant according to the present invention which has five adsorbers 10 operating in parallel. Although the present invention can function with a single adsorber it is preferred, the reasons which will become apparent below, to have a plurality of adsorbers 10.

Water to be treated flows from water inlet 12 through inlet line 14 to the inlet 13 of each of the adsorbers 10. The water supplied normally comes from a ground water source. The inlet line 14 has an inlet branch 16 to each of the adsorbers 10. Each inlet branch 16 includes an inlet control

valve 18 which is controllable to allow water flow into the particular adsorber 10 to which respective branch 16 extends. The water inlet 12 may be diverted around the plant via a dedicated bypass line.

In the illustrated embodiment the water inlet 12 is supplied from a mixing tank (not shown) upstream of the water inlet 12.

Each inlet control valve 18 is arranged to allow a predetermined rate of water flow into the respective adsorber 10. Water flow through inlet branch 16 will be prevented in certain instances, for example during backwashing cycles of the adsorber 10 and commissioning cycles of the adsorber 10 as explained in more detail below. In other cases the inlet control valve 18 is adjusted to provide a proportion of the water to be treated into the adsorber 10.

15

5

10

Each adsorber 10 has a water outlet 20 opening into an outlet line 22 via a respective outlet branch line 24. Each outlet branch line 24 is provided with an outlet branch valve 25 between the adsorber outlet 20 and the outlet line 22.

20

25

30

The illustrated plant is also provided with backwash and conditioning wash cycles for backwashing and conditioning washes of the adsorber 10. In the illustrated embodiment the water is arranged to flow substantially in the reverse direction through each adsorber 10 in backwashing cycles. In the illustrated embodiment, the inlets for the backwashing and conditioning washes are formed from the adsorbers outlets 20 and the outlet for the backwashing and conditioning water is formed through the water inlet 13 in the adsorber 10. Thus, the inlet/outlet 13,20 in the adsorber 10 perform multiple functions and this is advantageous in reducing the required ports into the adsorber 10. This is preferred in the present invention though of course separate inlet/outlets could be provided for in each washing cycle or

the backwashing and conditioning washes may have a separate inlet and outlets compared to the normal wash cycles which may be advantageous where the flow rate and volumes between backwashing and normal operation are particularly different.

5

In the illustrated embodiment the backwash inlet line 30 is fed from backwash pumps 32. The backwash line 30 has backwash inlet line branches 34 to each adsorber 10. The backwash line 30 is also used for conditioning washes.

10

15

Each backwash inlet line branch 34 opens into the respective outlet branch line 24 between the adsorber outlet 20 and the outlet branch line valve 25. The backwash inlet line branch 34 has a backwash inlet line valve 36 immediately before opening into the outlet line branch 24. This valve 36 prevents water flow through the backwash when the inlet line branch 34 is in normal operating cycle; and, as will be apparent operates in conjunction with outlet line branch valve 25 to allow water flow through the backwash line 30, 34 in backwashing and in conditioning cycles whilst at the same time valve 25 prevents flow through outlet branch line 24 to the outlet line 22.

25

30

20

In a backwashing cycle and conditioning wash cycles, water is outlet from the adsorber 10 through the water inlet 13. A backwash-outlet line 38 is linked to each adsorber via backwash outlet line branch 37. The inlet control valve 18 is provided in the inlet line branch 16 which is closed during backwashing and conditioning cycles to prevent water flow towards the water inlet 12. A corresponding backwash outlet branch valve 39 is provided in the backwash-outlet branch 37 which prevents flow through this line 37 during normal cycles of the apparatus, but allows water flow through this line 37 during backwash and conditioning wash cycles. The inlet line branch 16 opens into the backwash outlet branch line 37 between the valve

19 and the inlet 13.

- 5

10

15

20

25

30

Each backwash-outlet line branch 37 opens into the backwash outlet line 38 which feeds either into a holding tank 40 or directly to a waste outlet, e.g. a sewer 42. In backwashing cycles, the apparatus is normally designed to feed into the holding tank 40 which is provided as a settlement tank to allow particulate matter washed out of the adsorbers 10 to settle. The tank 40 is provided with a top water draw-off device and the cleaned water from which outputs to the water outlet 42. A pump can be provided to pump the water from out of the holding tank 40 if desired.

In the conditioning washing cycles of the apparatus, the conditioning wash waters are directed directly to the outlet 42 through a filter arrangement 44. In conditioning washes, considerably more particular matter is washed out of the adsorbers and the use of the filter cartridges 46 therefore removes this particulate matter before the water is outlet to waste. There are of course requirements on the quality of water allowed to pass to waste. Use of the cartridge filter then means that the cartridge can then be removed after a conditioning cycle and disposed of separately. It has an advantage in so far as the holding tank volume can be greatly reduced if it does not have to be used for conditioning washes as well as back washes.

Exploded cross-sections of the adsorbers 10 are shown in figure 2. From figure 2 it is clear that in the illustrated embodiment the adsorber 10 comprises a substantially cylindrical casket with domed closures at the top and bottom. The adsorber 10 has an inlet 13 and an outlet 20 through which water is pumped through the chamber. In normal cycle, water enters through the inlet 13, passes down the chamber to the outlet 20. In backwashing and conditioning cycles water mainly through the outlet 20 and exits via the inlet 13, though of course in forward flush modes water travels in the same direction as the normal cycle. The adsorber 10 includes a base

62 which supports a media column 64. The base is located above the outlet 20. The column 64 extends from the base 62 to just below the inlet 13. The media column 64 comprises a thin layer of gravel 68 over which particulate adsorption media 66 rests. The adsorption media 66 must adsorb arsenic thereonto from water.

In the illustrated embodiment the adsorption media 66 is a particulate ferric oxide material produced from a naturally mined ore. This has been treated to have an average diameter of less than 2mm and more than 0.25 mm. In the illustrated embodiment, less than 10% of the granules have a diameter greater than 2 mm and less than 5% of the granules have a diameter of less than 0.25 mm. The average diameter is approximately 0.8 mm. In the granulization process of the natural material, the grain density is adjusted to between 1 and 2 kg/dm³ and is preferably in the region of 1.58 kg/dm³. The average bulk density at 45% water content should be above 1.1 g/cm³, but no more than 1.4 g/cm³. The bulk density in the illustrated embodiment is controlled to 1.25 g/cm³. The granules are controlled to have a particular surface about $1.6 \times 10^{-5} \text{m}^2/\text{dm}^3$. The natural material contains at least 50% by weight iron. The granulated ferric material of this nature has a very high adsorption of arsenic which allows unprecedently long bed lifes. Also through the control of the properties as described above, the material is substantially more robust than untreated material which allows it to be handled and used. The untreated material has been found to smash when pouring into adsorbers and can not form a useable media bed.

25

30

20

5

10

15

Alternatively the granulated ferric material is formed synthetically. The synthetic material will be treated to produce similar robustness and surface features to allow the high adsorption and handability of the naturally formed material. The naturally produced material is slightly preferred at present in view of the cost of a naturally produced material compared to a synthetic material. However, it is expected that synthetic manufacturing processes

will be able to produce a synthetic material at an acceptable cost for commercial situations, even though they may be about 20% also more expensive than a naturally formed material. The advantages of a synthetic material are that the adsorption capacity may be even higher than a naturally produced material in view of the purity of the synthetic constituents. Table 1 shows the constituents of a preferred synthetic material which may be used as the adsorption media 66.

The gravel base layer 68 is put into the media column on the base 62 in order to prevent the granulated material 66 being washed from the adsorber 10 through the base 62. The base 62 must be provided with through openings 63 in order to allow backwashing flow and thus the small granular size ferric material may be washed through these openings 63. This immediate layer 68 of gravel prevents such loss. Of course, other supports could be used instead of gravel. The base 62 may be provided with nozzle openings 63 on a platform or alternatively may comprise a header and lateral pipework arrangement fitted with either mesh sleeves or nozzles.

Turning now to Figure 2, it will be clear that there are several ports into the adsorber 10. There is a manway 72 located about half way down the chamber. This is provided to allow access to the interior of the chamber. There are sight glasses 74, 76 located to allow visual inspection of the interior of the chamber. Main port 78 is provided to allow the media to be poured into the chamber from the top thereof. There is also a main outlet port 80 provided to allow access to the underside of the nozzle plate, next thereto is a smaller port 82 to act as a drain outlet.

Above the main inlet port 78 a davit 90 is provided which is used when filling the chamber with the media columns 64.

The adsorber 10 is supported on four legs 88.

5

10

15

20

25

Each of the adsorbers 10 are substantially the same as in the illustrated embodiment, though sizes and detailed construction may vary in particular installations.

It is preferred to have a plurality of adsorbers, rather than a single larger adsorber. The plurality of adsorbers allows one of the adsorbers to be taken offline, e.g. for backwashing and refilling of media column 64, whilst the other adsorbers take the flow which would normally be processed by the adsorber taken out of line.

10

15

The present invention relates to an apparatus and method for removal of arsenic or other metal salts from drinking water. The invention uses a bed of granulated ferric hydroxide to adsorp the metal in a pressurized adsorption chamber. The bed is sized to about 10m^3 and run with an EBCT of about 3 minutes which has been found to give an unprecedently long bed life of upto 200,000 bed volumes of treated water.

and a

TECHNICAL SPECIFICATION FOR GRANULAR FERRIC HYDROXIDE

Table 1

Property	Minimum	Maximum	Typical
Grain Deneity (Kg/dm ³)	1.55	1.6	1.58
Bulk Density (g/cm³) (at 45% Water Content)	1.22	1.29	1.25
Bulk Porosity	22	28	25
Sieve Analysis: <0.32 mm >2.0 mm	- 105	5% 10%	3% 5% 1.6 x 10 ⁴
Specific Surface (m²/dm³) Chemical Analysis:	1.6 x 10 ^s		1,0 % 10
As Pb Cd Cr Cu Fe Mn		-	<pre><5 mg/kg 10 mg/kg 2 mg/kg 150 mg/kg 30 mg/kg 500 g/kg 2300 mg/kg 150 mg/kg</pre>
Ni Zn	-	_ \	150 mg/kg

Further to the above table of properties, the GFH will be soaked for 8 hours in distilled water, whereupon metals analysis will be performed on the membrane filtered 0.45 µm (micrometer) Leachate. Leachate concentrations must be less than those shown below:

Maximum Metal Concentrations (µg/i)

Aluminium	60	Lead	3
Antimony	3	Manganese	15
Arsenic	7	Mercury	0.3
Barium	300	Nickel	15
Cadmium	1.5	Selenium	3
Chromium	15	Silver	3
lron	3000		

5

10

CLAIMS:

- 1. An apparatus for removing metals from water comprising an adsorption chamber including a bed having a bed height and comprising a ferric material, a water inlet connectable to a first water supply on one side of the bed, a water outlet on the other side of the bed and a backwash inlet connectable to a second water supply on the said other side of the bed, the apparatus being arranged for normal and backwash operations, in normal operation arsenic is adsorbed onto the bed from water flowing from the said one side to said other side, and in backwash operation water flows from the backwash inlet to said one side of the bed, the bed height is between 0.5m and 2.0m and the empty bed contact time (EBCT) is between 1 and 6 minutes.
- The apparatus according to claim 1, wherein the bed has a bed volume and the apparatus is arranged for at least 10,000, preferably 30,000 and more preferably 60,000, bed volume of water to be treated in normal operations between backwash operations.
- 3. The apparatus according to claim 2, wherein the backwash operation comprises about 10 bed volumes of water, preferably 5 bed volumes of water.
- 4. The apparatus according to any one of claims 1 to 3, wherein the backwash operation has a flow rate of less than 50m/h, preferably equal to or less than 30 m/h.
 - 5. The apparatus according to any one of claims 1 to 4, wherein a forward flush immediately precedes a backwash operation.
 - 6. The apparatus according to claim 5, wherein the forward flush

comprises about 10 bed volumes of water, preferably about 5 bed volumes of water.

7. The apparatus according to claim 5 or claim 6, wherein the forward flush comprises flushing water from the second supply from the said one side of the bed to the said other side of the bed.

5

10

20

25

BNSDGGID: <WO 0162670A1_i_>

- 8. The apparatus according to any one of claims 5 to 7, wherein the forward flush has a flow rate of less than 30 m/h, preferably less than 25 m/h.
 - 9. The apparatus according to any one of claims 1 to 8, wherein the adsorption chamber includes a base arranged to support the bed.
- 15 10. The apparatus according to claim 9, wherein the base includes openings.
 - 11. The apparatus according to claim 9 or claim 10, wherein the base comprises a wedgewire material.

«رايه زيان

- 12. The apparatus according to any one of claims 1 to 11, wherein the ferric material comprises a granular ferric material, the material having an average diameter of less than 2mm and more than 0.25mm, preferably less than 10% of the granules of diameter greater than 2mm and/or less than 5% of the granules of diameter less than 0.25mm.
 - 13. The apparatus according to claim 12, wherein the granular ferric material has an average diameter of about 0.8mm.
- 30 14. The apparatus according to claim 12 or claim 13, wherein the material is a granulated natural material.

5

10

15

25

- 15. The apparatus according to any one of claims 1 to 14, wherein the material comprises ferric hydroxide.
- 16. The apparatus according to any one of claims 12 to 15, wherein the grain density is between 1 to 2 kg/dm³, preferably 1.5 to 1.7 kg/dm³ and more preferably in the region of 1.58 kg/dm³.
 - 17. The apparatus according to any one of claims 12 to 16, wherein the average bulk density at 45% water content is at least 1.1g/cm³ and/or no more than 1.4g/cm³, and preferably between 1.2 and 1.3 g/cm³, more preferably in the region of 1.25g/cm³.
 - 18. The apparatus according to any one of claims 12 to 17, wherein the material has a specific surface of about $1.6 \times 10^5 \text{m}^2/\text{dm}^3$.
 - 19. The apparatus according to any one of claims 1 to 18, wherein the material comprises at least 50% by weight iron.
- 20. The apparatus according to any one of claims 12 to 19, wherein the bed includes a layer of gravel of greater average diameter than the ferric material.
 - 21. The apparatus according to any one of the preceding claims where the metal is selected from the group consisting of arsenic; copper; cadmium, nickel; chromium; silver; lead; molybdenum; manganese; and mixtures thereof.
 - 22. The apparatus according to any one of the preceding claims, wherein the bed has a bed volume and the ferric material is replaced after at least 100,000 bed volumes of water have been treated in normal operation, preferably at least 120,000 bed volumes and more preferably at least

5

15

25

30

150,000 bed volumes.

- 23. The apparatus according to any one of the preceding claims, wherein the Ph in bed in the adsorption chamber is normal operation is the range of 7.0 and 8.5 preferably 7.5 and 8.0, and more preferably in the region of 7.8.
- 24. The apparatus according to any one of the preceding claims, wherein the bed is at least 1m in height and the bed has a volume of about 10m³.
- 10 25. The apparatus according to any one of the preceding claims, wherein the apparatus is arranged to provide a conditioning cycle when new bed material is added to the adsorption chamber, wherein the conditioning cycle comprises an initial bed stratification backwash conditioning backwash and a final conditioning forward flush.
 - 26. The apparatus according to claim 25, wherein the initial bed stratification backwash comprises about 4 bed volumes of water at about 30m/h.
- 20 27. The apparatus according to claim 25 or claim 26, wherein the final conditioning backwash comprises a backwash cycle as defined in any of the preceding claims.
 - 28. The apparatus according to any one of claims 25 to 27, wherein the conditioning forward flush comprises a forward flush as herein before defined.
 - 29. The apparatus according to any one of the preceding claims, wherein the apparatus is arranged to provide a loading backwash of about 10 bed volumes of water at less than 10m/h e.g. about 5m/h, when loading the bed material into the adsorption chamber.

30. The apparatus according to any one of the preceding claims, wherein the apparatus includes a plurality of similar adsorption chambers having shared first water supplies and second water supplies.

- 5 31. The apparatus of claim 30, wherein at most 1 of the adsorption chamber is undergoing any backwash cycle or forward flush at any one time.
- 32. The apparatus according to claim 30 or claim 31, wherein the adsorption chambers are split into first and second groups and the first water supply is arranged to supply water at different rates to the first and second groups.
- 33. The apparatus according to any one of the preceding claims, wherein either: a) the rate of water through the bed in normal operation is less than 50m/h, preferably less than 30m/h, and more preferably about 25m/h.
 - 34. The apparatus according to any one of the preceding claims, wherein the EBCT in normal operation is in the region of 3 minutes.
- 20 35. A process for removing metal from water comprising the steps of:

 a) providing a bed of ferric material having a bed height of between

 0.5 and 2.0m;

25

30

ENISDOCIDI - MICH DI 1997/04 1 | 5

- b) in normal operation supplying water from a first water supply from one side of the bed to the other side of the bed such that arsenic is adsorbed from the water onto the bed;
- c) in backwash operation supplying water from a second water supply from said other side of the bed to said one side of the bed so as to remove contaminating material from the bed without substantially disrupting the media; wherein in normal operation, the empty bed contact time for said water is between 1 and 6 minutes.

36. The process according to claim 35, wherein at least 10,000, preferably 30,000 and more preferably 60,000, bed volume of water are treated in normal operation between backwash operations.

- 5 37. The process according to claim 35 or claim 36, wherein the backwash operation comprises about 10 bed volumes of water, preferably 5 bed volumes of water.
- 38. The process according to any one of claims 35 to 37, wherein the backwash operation has a flow rate of less than 50m/h, preferably equal to or less than 30 m/h.
 - 39. The process according to any one of claims 35 to 38, wherein a forward flush immediately precedes a backwash operation.
 - 40. The process according to claim 39, wherein the forward flush comprises about 10 bed volumes of water, preferably about 5 bed volumes of water.
- 20 41. The process according to claim 39 or claim 40, wherein the forward flush comprises flushing water from the second supply from the said one side of the bed to the said other side of the bed.
- 42. The process according to any one of claims 39 to 41, wherein the forward flush has a flow rate of less than 30 m/h, preferably less than 25 m/h.
 - 43. The process according to any one of claims 35 to 42, wherein the bed is supported on a base.
 - 44. The process according to claim 43, wherein the base includes

30

openings.

45. The process according to claim 43 or claim 44, wherein the base comprises a wedgewire material.

5

10

- 46. The process according to any one of claims 35 to 46, wherein the ferric material comprises a granular ferric material, the material having an average diameter of less than 2mm and more than 0.25mm, preferably less than 10% of the granules of diameter greater than 2mm and/or less than 5% of the granules of diameter less than 0.25mm.
- 47. The process according to claim 46, wherein the granular ferric material has an average diameter of about 0.8mm.
- 15 48. The process according to claim 46 or claim 47, wherein the material is a granulated natural material.
 - 49. The process according to any one of claims 46 to 48, wherein the material comprises ferric hydroxide.

- 50. The process according to any one of claims 12 to 15, wherein the grain density is between 1 to 2 kg/dm^3 , preferably 1.5 to 1.7 kg/dm³ and more preferably in the region of 1.58 kg/dm³.
- 51. The process according to any one of claims 46 to 50, wherein the average bulk density at 45% water content is at least 1.1g/cm³ and/or no more than 1.4g/cm³, and preferably between 1.2 and 1.3 g/cm³, more preferably in the region of 1.25g/cm³.
- 30 52. The apparatus according to any one of claims 46 to 51, wherein the material has a specific surface of about $1.6 \times 10^5 \text{m}^2/\text{dm}^3$.

53. The process according to any one of claims 35 to 52, wherein the material comprises at least 50% by weight iron.

- 54. The process according to any one of claims 46 to 52, wherein the bed includes a layer of gravel of greater average diameter than the ferric material.
- 55. The process according to any one of claims 35 to 54, wherein the metal removed from the water is selected from the group consisting of: arsenic; copper; cadmium; nickel; chromium; silver; lead molybdenum and mercury.
- 56. The method according to any one of claims 35 to 55, wherein the ferric material is replaced after at least 100,000 bed volumes of water have been treated in normal operation, preferably at least 120,000 bed volumes and more preferably at least 150,000 bed volumes.
- 57. The process according to any one of claims 35 to 56, wherein the pH in bed in the adsorption chamber is normal operation is the range of 7.0 to 8.5 preferably 7.5 to 8.0 and more preferably in the region of 7.8.
- 58. The process according to any one of claims 35 to 57, wherein the bed height is at least 1m.
- 59. The process according to any one of claims 35 to 58, wherein the process includes a step d) comprising a conditioning cycle when new bed material is added to process, wherein the conditioning cycle comprises an initial bed stratification backwash, a final conditioning backwash and a final conditioning forward flush.
- 30 60. The process according to claim 59, wherein the initial bed stratification backwash comprises about 4 bed volumes of water at about

5

10

15

20

30m/h.

- 61. The process according to claim 59 or claim 60, wherein the final conditioning backwash comprises a backwash cycle as defined in any of the preceding claims 35 to 60.
- 62. The process according to any one of claims 59 to 61, wherein the conditioning forward flush comprises a forward flush as herein before defined in claims 39 to 42.

10

5

63. The process according to any one of claims 34 to 62, wherein the process further includes the step e) comprising: a loading backwash of about [m] bed volumes of water at less than 10m/h e.g. about 5m/h, when loading the bed material into the process chamber.

15

64. The process according to any one of claims 34 to 63, wherein the bed is provided in an adsorption chamber and the method is conducted simultaneously in a plurality of similar adsorption chambers having shared first water supplies and second water supplies.

20

65. The process of claim 64, wherein at most 1 of the adsorption chambers is undergoing any backwash cycle or forward flush at any one time.

- 66. The process according to claim 64 or claim 65, wherein the adsorption chambers are split into first and second groups and the first water supply is arranged to supply water at different rates to the first and second groups.
- 30
- 67. The process according to any one of claims 35 to 66, wherein in step b) the water through the bed is less than 50m/h, preferably less than 30m/h,

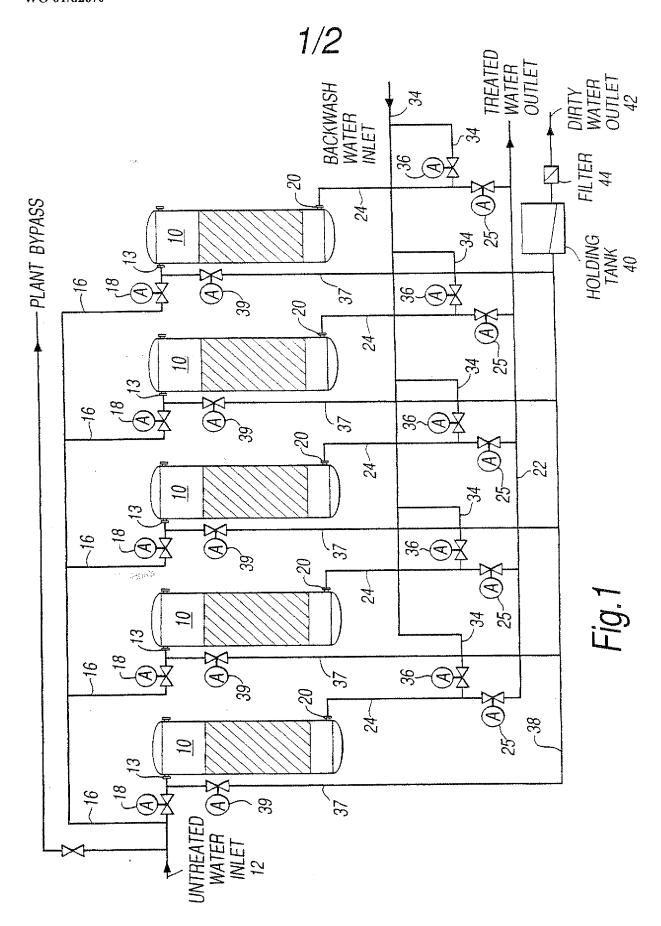
and more preferably about 25m/h.

68. The process according to any one of claims 35 to 67, wherein the empty bed contact time [EBCT] is normal operation in between 1.5 and 6 minutes and preferably about 3 minutes.

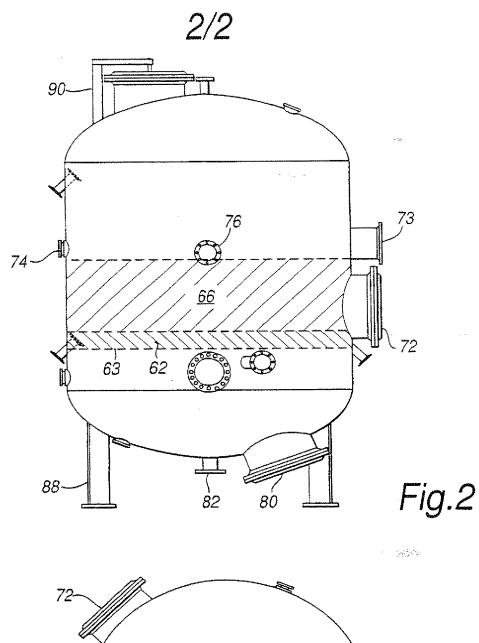
- 69. The process according to any one of claims 35 to 68, wherein the bed volume is about $10m^3$.
- 70. An apparatus for removing arsenic from water as hereinbefore described with reference to and/or as illustrated by the accompanying drawings.
- 71. A process for removing arsenic from water as hereinbefore described with reference to and/or as illustrated by the accompanying drawings.

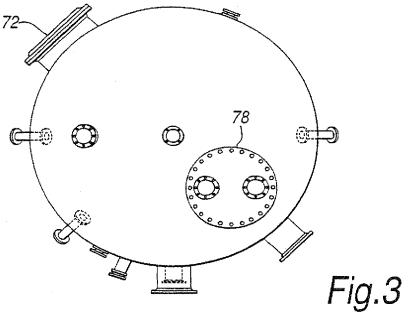
31.25 V

1000



SUBSTITUTE SHEET (RULE 26)





SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

ir national Application No PCT/GB 01/00822

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 CO2F1/28 //CO2F101/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC $\frac{7}{2}$ CO2F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical search terms used)

EPO-Internal, PAJ, WPI Data

Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No	
US 4 414 115 A (THE PAUL J) 8 November 1983 (1983-11-08)	1,10-14, 16-21, 24,70	
the whole document	30,32 35-69,71	
DE 43 20 003 A (JEKEL MARTIN PROF DR ING) 15 December 1994 (1994-12-15)	1,2, 12-21, 24,70	
example	9,10,30, 32,66 35-65,	
	67-69	
US 4 565 633 A (MAYENKAR KRISHNA V) 21 January 1986 (1986-01-21)	9,10,30, 32,66 1,12+21,	
the whole document	24	
	US 4 414 115 A (THE PAUL J) 8 November 1983 (1983-11-08) the whole document DE 43 20 003 A (JEKEL MARTIN PROF DR ING) 15 December 1994 (1994-12-15) example US 4 565 633 A (MAYENKAR KRISHNA V)	

X Further documents are listed in the continuation of box C.	Yatent tamily members are tisted in annex.
A document defining the general state of the lart which is not considered to be of particular relevance. E* earlier document but published on or after the international filling date. L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified). O* document reterring to an oral disclosure, use, exhibition or other means. P* document published prior to the international filling date but	 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention. "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone. "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "8" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
10 July 2001	20/07/2001
Name and mailing address of the ISA	Authorized officer
European Palent Office, P.B. 5818 Palentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Gruber, M

Form PCT ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

r ational Application No PCT/GB 01/00822

	nion) DOCUMENTS CONSIDERED TO BE RELEVANT	Relevant to claim No.
Lategory :	Gilation of document, with indication, where appropriate, of the relevant passages	Traiblant to outstand
X .	PATENT ABSTRACTS OF JAPAN vol. 011, no. 349 (C-456), 14 November 1987 (1987-11-14) & JP 62 121690 A (DOWA KOEI KK), 2 June 1987 (1987-06-02) abstract -& DATABASE WPI Section Ch, Week 198727, 2 June 1987 (1987-06-02) Derwent Publications Ltd., London, GB; Class D15, AN 1987-190206 XP002169873 abstract	1,20,21, 35, 53-55, 58,70,71
A	DE 197 45 664 A (ES HA ES ANLAGENSTEUERUNGEN AU) 29 April 1999 (1999-04-29) the whole document	1,12-21, 35,70,71
A	CA 1 067 627 A (NOVA SCOTIA RES FOUND) 4 December 1979 (1979-12-04) the whole document	
А	WO 99 50182 A (ALCAN INT LTD ; AZIZIAN FARID (GB)) 7 October 1999 (1999-10-07) claims	
A	DE 42 14 487 A (WAHNBACHTALSPERRENVERBAND) 18 November 1993 (1993-11-18) the whole document	
A	US 5 369 072 A (CHANG YU-JUNG ET AL) 29 November 1994 (1994-11-29) the whole document	
A	JP 52 133890 A (UENO KAGEHIRA) 9 November 1977 (1977-11-09) -& DATABASE WPI Week 197751, 9 November 1977 (1977-11-09) Derwent Publications Ltd., London, GB; AN 1977-90982y XP002169874 abstract	
A	US 5 126 048 A (ZHANG YUN H) 30 June 1992 (1992-06-30) the whole document	
A	US 5 368 739 A (DUSSERT BERTRAND W ET AL) 29 November 1994 (1994-11-29) the whole document	
A	US 4 752 397 A (SOOD AJAY) 21 Juhe 1988 (1988-06-21) the whole document	

INTERNATIONAL SEARCH REPORT

Information on patent family members

ir national Application No PUT/GB 01/00822

Patent document cited in search report		Publication date	Patent family member(s)		Publication date	
US	4414115	Α	08-11-1983	NONE		
DE	4320003	Α	15-12-1994	NONE		
us us	4565633	Α	21-01-1986	NONE	منت جمع المناس المنت المناس	anne alle mai anne anne anne anne alle alle alle alle
JP	62121690	Α	02-06-1987	NONE	an annual alaksi sagan gapan annu annu alaksi katun sagan alaksi sagan alaksi katun sagan alaksi sagan alaksi s	
DE	19745664	A	29-04-1999	NONE		
CA	1067627	A	04-12-1979	NONE	alle Manne Manne sylvis skiller genne skilar kanne kilar kalle Manne gene belike sal	na mana makankulun mana, manga apina dalah urum urum kalah dalah 1888 MBM MBM MBM
WO	9950182	A	07-10-1999	AU BR EP	3429399 A 9909332 A 1070019 A	18-10-1999 12-12-2000 24-01-2001
DE	4214487	Α	18-11-1993	NONE		
US	5369072	Α	29-11-1994	US	5911882 A	15-06-1999
JF	52133890	A	09-11-1977	JP JP	1077135 C 56022578 B	25-12-1981 26-05-1981
US	5 5126048	Α	30-06-1992	US GB JP JP JP	5075010 A 2250983 A,B 1999591 C 4267995 A 7034911 B	24-12-1991 24-06-1992 08-12-1995 24-09-1992 19-04-1995
U	S 5368739	A	29-11-1994	US US	5368738 A 5466378 A	29-11-1994 14-11-1995
— U	S 4752397	Α	21-06-1988	NONE		MI WAS

...